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The *situ* preparation of silica nanoparticles on the surface of functionalized graphene nanoplatelets

Jiani Li, Kejing Yu*, Kun Qian, Haijian Cao, Xuefeng Lu and Jie Sun

Abstract

A method for *situ* preparing a hybrid material consisting of silica nanoparticles (SiO_2) attached onto the surface of functionalized graphene nanoplatelets (f-GNPs) is proposed. Firstly, polyacrylic acid (PAA) was grafted to the surface of f-GNPs to increase reacting sites, and then 3-aminopropyltriethoxysilane (APTES) KH550 reacted with abovementioned product PAA-GNPs to obtain siloxane-GNPs, thus providing reaction sites for the growth of SiO_2 on the surface of GNPs. Finally, the SiO_2 /graphene nanoplatelets (SiO_2 /GNPs) hybrid material is obtained through introducing siloxane-GNPs into a solution of tetraethyl orthosilicate, ammonia and ethanol for hours' reaction. The results from Fourier transform infrared spectroscopy (FTIR) showed that SiO_2 particles have *situ* grown on the surface of GNPs through chemical bonds as Si-O-Si. And the nanostructure of hybrid materials was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). All the images indicated that SiO_2 particles with similar sizes were grafted on the surface of graphene nanoplatelets successfully. And TEM images also showed the whole growth process of SiO_2 particles on the surface of graphene as time grows. Moreover, TGA traces suggested the SiO_2 /GNPs hybrid material had stable thermal stability. And at 900°C , the residual weight fraction of polymer on siloxane-GNPs was about 94.2% and that of SiO_2 particles on hybrid materials was about 75.0%. However, the result of Raman spectroscopy showed that carbon atoms of graphene nanoplatelets became much more disordered, due to the destroyed carbon domains during the process of chemical drafting. Through orthogonal experiments, hybrid materials with various sizes of SiO_2 particles were prepared, thus achieving the particle sizes controllable. And the factors' level of significance is as follows: the quantity of ammonia > the quantity of tetraethyl orthosilicate (TEOS) > the reaction time.

Keywords: Graphene; SiO_2 particles; Hybrid material; *Situ* preparation; Controllability

Background

Graphene, a single layer carbon material in a close arrangement of honeycomb two-dimensional lattice [1], has remarkable properties, such as Young's modulus, fracture strength, specific surface area and so on [2-4]. Significantly, graphene is a promising building block material for composites because of its large surface area. Furthermore, decoration of the graphene nanosheets with organic/inorganic materials can bring about an important kind of graphene-based composites [5-10]. However, the two-dimensional structure and huge specific surface area of graphene nanoplatelets made it easy to aggregate, which limited its application [11]. Thus it is necessary to overcome graphene's extreme hydrophobicity which leads to aggregation in polar liquids [12,13].

Researches indicated that the modification of graphene nanoplatelets is arguably the most versatile and easily scalable method [14]. Meaningfully, the decoration of nanomaterials onto graphene nanosheets is helpful to overcome the aggregation of individual graphene nanosheets and nanomaterials themselves [15]. In recent years, researchers have shown an increasing interest in graphene-based composites [16,17] in which graphene sheets are used as a wild phase to enhance mechanical properties [18]. Among all these materials, hybrid materials based on GNPs and silica nanoparticles have attracted significant scientific interest because of their remarkable properties that do not exist in the individual components [19-22]. Due to the synergistic effect, graphene nanoplatelets/ SiO_2 hybrid materials have superior properties compared with bare graphene nanoplatelets and SiO_2 particles [23]. Considering the outstanding properties of graphene nanoplatelets and SiO_2 , graphene/silica composite would be one

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of the greatly popular and interest topics in the field of nanomaterial and nanotechnology [24]. And this kind of composite materials have been explored as adsorbents [25,26], catalysts [27], and fillers into resin for composites along with an excellent application potential [28,29].

Hao [11] et al. prepared SiO₂/graphene composite for highly selective adsorption of Pb (II) ion through a simple two-step reaction, including the preparation of SiO₂/graphene oxide and the reduction of graphene oxide (GO). Zhou [24] et al. used a one-pot hydrothermal synthesis to obtain a mesoporous SiO₂-graphene hybrid from tetraethyl orthosilicate and graphene oxide without any surfactant. Lu [30] et al. reported on the preparation of well-defined SiO₂-coated graphene oxide (GO) nanosheets (SiO₂/GO) without prior GO functionalization by combining sonication with solgel technique. And then, the product is decorated with Ag nanoparticles for H₂O₂ and glucose detection. However, all these abovementioned method did not have the advantage of controlling the size of SiO₂. Accordingly, the development of new preparation strategy overcoming the shortcoming is highly desired.

In our previous work, we introduced an easy and facial methodology to prepare functionalized graphene nanoplatelets (f-GNPs/SiO₂) hybrid materials, using polyacryloyl chloride (PACl) as the bridge to connect graphene platelets and SiO₂ particles. We have also introduced a facile approach to prepare multiwalled carbon nanotubes/graphene nanoplatelets hybrid materials. In this paper, we proposed a strategy to *situ* prepare SiO₂ particles with similar sizes onto the surface of graphene

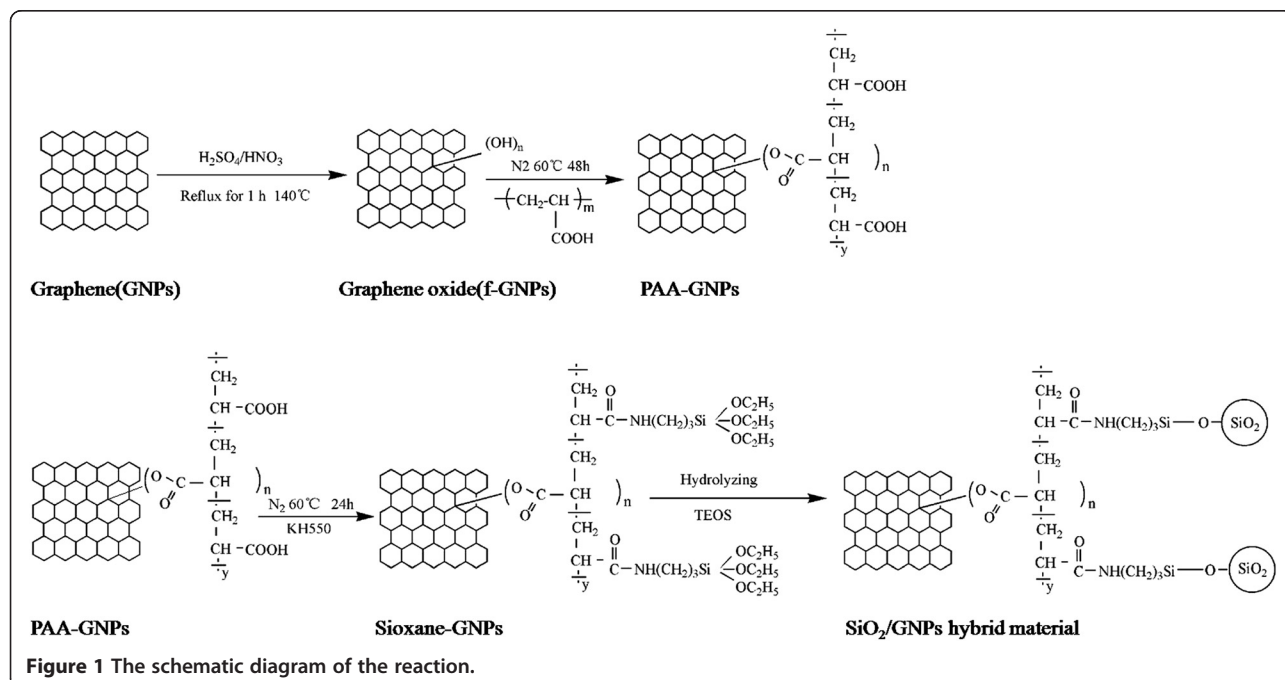
nanosheets. The schematic diagram of reaction is illustrated in Figure 1. At first step, graphene nanosheet was acid treated by H₂SO₄/HNO₃ (30 ml/30 ml) at 140°C for 1 h. Then, polyacrylic acid (PAA) was grafted onto the surface of f-GNPs through chemical bond C-O. And KH550 reacted with above mention product PAA-GNPs through chemical bond C-C=O to obtain siloxane-GNPs. Finally, the SiO₂/GNPs hybrid material is produced through introducing siloxane-GNPs into a solution of tetraethyl orthosilicate, ammonia and ethanol for hours' reaction. This approach is easy to control and efficient. Meaningfully, the size of situ general silica nanoparticles could be readily controlled by adjusting the ammonia concentration in the aqueous solution and the reaction time. There are various factors that can affect the size of SiO₂ particles [31]. In present work, through orthogonal experimental design [32], we discuss the impact of following three factors on the size of SiO₂ particles: the quantity of tetraethyl orthosilicate (TEOS), the quantity of ammonia and the reaction time.

Methods

Experimental section

Materials

Graphene nanoplatelets (GNPs) (diameter, 1 to 20 μm; thickness, 5 to 15 nm) were purchased from Xiamen Kona Graphene Technology Co., Ltd. (Xiamen, China). PAA (PH: 1–2) was purchased from Tianjin Damao chemical reagent Co. Ltd. N,N-Dicyclohexyl carbodiimide (DCC) was purchased from Aladdin industrial corporation, Seattle, Washington D.C., USA. 3-Aminopropyltriethoxysilane



(APTES) KH550 was purchased from Shanghai Yaohua Chemical Co. Ltd., Shanghai, China. H_2SO_4 (98%), HNO_3 (65%), tetrahydrofuran (analytically pure), TEOS (AR), ammonia solution (AR), and ethanol (AR) were provided by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

Oxidation of graphene nanoplatelets

GNPs (900 mg) were suspended and refluxed in a mixture of concentrated acid $\text{H}_2\text{SO}_4/\text{HNO}_3$ (30 ml/30 ml) at 140°C for 1 h, followed by diluting with deionized water (3,000 ml). The acid-treated GNPs were retrieved and washed repeatedly with THF until pH = 7 and dried under vacuum. The product was denoted as f-GNPs.

Grafting PAA onto f-GNPs

f-GNPs 50 mg, PAA 100 mg, DCC 100 mg, and THF 50 ml were mixed under dry nitrogen atmosphere and then stirred in a flask for 48 h at 60°C . The solid product was collected and washed repeatedly with THF until pH = 7 and dried under vacuum. The product was denoted as PAAGNPs.

Reaction of PAA-GNPs and KH550

PAA-GNPs 100 mg, DCC 100 mg and THF 100 mg were mixed by sonication for 1 h. Then, the solution of KH550 was added dropwise into suspension at 60°C under nitrogen atmosphere. When completed, the reaction was kept at 60°C and vigorously stirred for 24 h. At last, the solid product was collected and washed repeatedly with THF until pH = 7 and dried under vacuum. The KH550 functionalized GNPs were denoted as siloxane-GNPs.

Preparation of SiO_2 /GNPs hybrid material

Siloxane-GNPs (50 mg) were added into 10 ml deionized water and stirred for 24 h at room temperature to hydrolyze the alkoxy silane into Si-OH. Then, 0.6 g TEOS, 1.2 g ammonia solution, and 100 ml ethanol were added to the suspension and stirred for 8 h. Finally, the solid product was collected and washed repeatedly with THF until pH = 7 and dried under vacuum. In this process, the quantity of TEOS, the quantity of ammonia, and the time of reaction can be different. Thus, we can control the size of SiO_2 particles.

Orthogonal array experimental design

In the present study, the experiment was based on an orthogonal array experimental design where the following three factors were analyzed: the quantity of TEOS, the quantity of ammonia and the reaction time. These variables were identified to have large effects on the growth of SiO_2 particles. So an orthogonal array of three factors and three levels was employed to assign the

considered factors and levels as shown in Table 1. In principle, one column could be assigned to a factor. Here, the matrix denotes three factors, each with three levels (Table 2). Data analysis could be carried out through the range analysis.

Characterizations

Fourier transform infrared spectrometer (FTIR, Nexus 670, Valencia, CA, USA) was used to detect the functional groups on the surface of f-GNPs and f-GNPs/ SiO_2 hybrid materials, which was measured as pellets with KBr. Raman spectroscopy (In Via laser confocal microscope, Renishaw, Wotton-under-Edge, UK) was employed to investigate the ordered or disordered crystal structures and assessing defects of samples, which was recorded using a spectrometer with 532 nm wavelength incident laser light. Thermal gravimetric analysis (TGA, SDTA851e) was used to evaluate the weight loss ratio of the products. The tests were conducted at a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C under nitrogen. Scanning electron microscopy (SEM, HITACHI SU1510, Chiyoda-ku, Japan) was employed to observe the surface morphology of various products, whose accelerating voltage was 1.0 kV. Transmission electron microscopy (TEM, H-800-1) was employed to observe the microstructure of various products, whose accelerating voltage was 20 kV.

Results and discussion

Fourier transform infrared spectroscopy

The FTIR spectra of f-GNPs, PAA-GNPs, siloxane-GNPs, and SiO_2 /GNPs hybrid material were presented in Figure 2. The peaks at $3,440\text{ cm}^{-1}$ (Figure 2a) which were attributed to stretching vibration of O-H groups could be observed clearly. The results indicated that GNPs had been functionalized successfully as designed. The peaks at $1,190$ and $1,100\text{ cm}^{-1}$ (Figure 2b) were assigned to stretching vibration of C-O-C groups between GNPs and PAA, which indicated that PAA was grafted onto the surface of GNPs successfully. As showed in Figure 3c, the peaks at $1,556$ and $3,300\text{ cm}^{-1}$ were attributed to bending vibration and stretching vibrating of N-H groups of amide, respectively. And the peak at $1,640\text{ cm}^{-1}$ (Figure 2c) was attributed to stretching vibration of C=O groups of amide. Meanwhile, the peaks at $1,121$ and $1,045\text{ cm}^{-1}$ were attributed to stretching vibrating of Si-O and C-O groups of siloxane respectively. Also, the peak at $2,930\text{ cm}^{-1}$

Table 1 Levels of factor of orthogonal design

Level	Factors		
	TEOS (g)	$\text{NH}_3 \cdot \text{H}_2\text{O}$ (g)	Time (h)
1	0.3	0.6	4
2	0.6	1.2	6
3	0.9	1.8	8

Table 2 Orthogonal arrays for statistical experiment and results

No.	Experiment conditions					Results
	Ethanol (ml)	Temperature (°C)	TEOS (g)	NH ₃ · H ₂ O (g)	Time (h)	Average particle size (nm)
1	100	30	0.3 (1)	0.6 (1)	4 (1)	50
2	100	30	0.3 (1)	1.2 (2)	6 (2)	120
3	100	30	0.3 (1)	1.8 (3)	8 (3)	140
4	100	30	0.6 (2)	0.6 (1)	6 (2)	100
5	100	30	0.6 (2)	1.2 (2)	8 (3)	240
6	100	30	0.6 (2)	1.8 (3)	4 (1)	170
7	100	30	0.9 (3)	0.6 (1)	8 (3)	130
8	100	30	0.9 (3)	1.2 (2)	4 (1)	160
9	100	30	0.9 (3)	1.8 (3)	6 (2)	280

was assigned to stretching vibration of C-H groups of alkyl groups. All these features confirmed that KH550 have linked with PAA-GNPs successfully. Figure 2d showed the spectrum of SiO₂/GNPs hybrid material, compared with Figure 2c; it was clear that there appeared new stretching vibration peak of Si-O-Si groups at about 1,096 cm⁻¹, and the peak at 796 cm⁻¹ was attributed to the symmetric stretching of Si-O-Si groups as designed in Figure 1. All these data indicated that SiO₂ fabricated on the surface of GNPs successfully.

Raman spectra

Raman spectroscopy is a powerful and useful technique to investigate the ordered or disordered crystal structures and assessing defects of graphene-based materials. It is well known that the typical features of carbon materials in Raman spectra are the G band at 1,580 cm⁻¹ deriving from the E_{2g} phonon of C sp² atoms and D band at 1,350 cm⁻¹ considered as a breathing mode of k-point photos of A_{1g} symmetry which is assigned to local defects and disorder mostly at the edges of f-GNP platelet [33,34].

Raman spectra of f-GNP and SiO₂/GNPs hybrid material were shown in Figure 3. The D band at 1,352 cm⁻¹ and G band at 1,580 cm⁻¹ of f-GNP could be seen clearly

in Figure 3a. While the D band at 1,308 cm⁻¹ and G band at 1,575 cm⁻¹ of f-GNPs/SiO₂ hybrid materials could be seen clearly in Figure 2b. The shifting (from 1,352 to 1,308 cm⁻¹) of D band was correlated with dramatic structural changes, associated with the changes of chemical bond between f-GNPs and SiO₂. According to our analysis, the I_D/I_G of f-GNPs and SiO₂/GNPs hybrid material was 0.814 and 1.145, respectively (Table 3). The intensity ratio of the D and G bands (I_D/I_G) is a measure of the reduction degree, which consists with the sp³/sp² carbon ratio, and the increasing in I_D/I_G demonstrated that sp³ or disordered carbon atoms increased and carbon domains were destroyed [35,36]. The increased I_D/I_G intensity ratio from 0.814 to 1.145 after chemical reaction could be attributed to covalent bond formation between f-GNPs and SiO₂ which could generate a considerable number of defect sites in the graphene structure. Thus, the Raman data suggested that after chemical reacting the surface of f-GNPs nanosheets was disordering seriously.

Thermal gravimetric analysis

Figure 4 presented the TGA curves for all the samples. As shown in Figure 3a, the raw SiO₂ kept stable without significant weight loss until 900°C. The final weight-loss

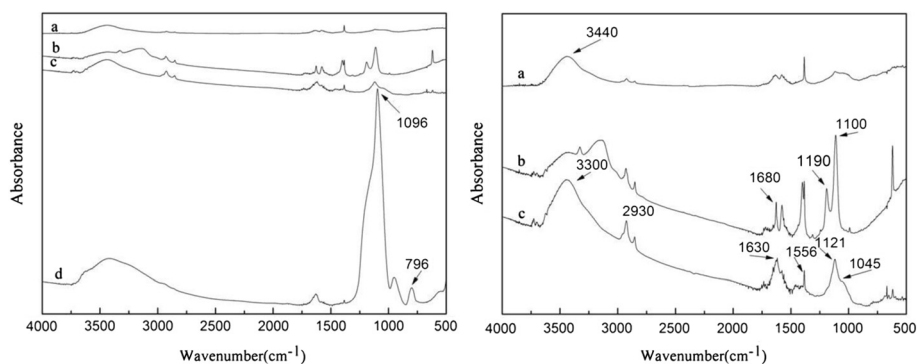


Figure 2 FTIR spectra of (a) f-GNPs, (b) PAA-GNPs, (c) siloxane-GNPs, and (d) SiO₂/GNPs hybrid material.

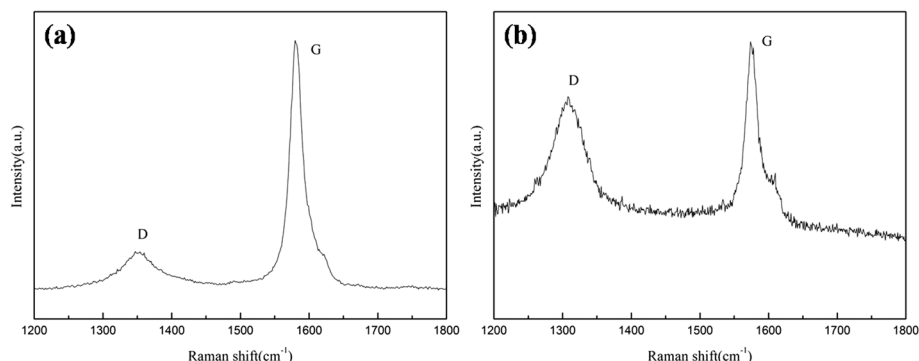


Figure 3 Raman spectra of (a) f-GNPs and (b) SiO₂/GNPs hybrid material.

ratio of neat SiO₂ particles was about 6.0%, which was caused by resolving of hydroxyl and carboxyl. Similarly, the f-GNPs (Figure 3b) kept stable without significant weight loss until 900°C, too. The final weight-loss ratio of f-GNPs was about 7.5%, which was caused by resolving of hydroxyl and carboxyl. SiO₂/GNPs hybrid material (trace c) kept stable without significant weight loss until 700°C, and it had a slight weight reduction from 700°C to 900°C as shown in Figure 4. SiO₂/GNPs hybrid material lost about 27% of its original weight in the end, which could be undoubtedly assigned to thermal decomposition of polymer. Thus, it suggested that the SiO₂/GNPs hybrid material we have prepared possessed stable thermal stability. As shown in Figure 4d, there was a shape reduction of weight and two stages of weight loss for siloxane-GNPs could be identified, the first stage from 200°C to 350°C and the second stage from 600°C to 880°C. The first stage was associated to the resolving of hydroxyl and carboxyl on the surface of f-GNPs and removal of the H₂O vapors of the sample; the major weight loss between 600°C and 880°C could be undoubtedly assigned to the decomposition of molecular chain of polymer. The final weight-loss ratio of siloxane-GNPs was about 90% in the end. PAA-KH550 polymer (trace e) lost about 95% of its original weight in the end, and two stages of weight loss for PAA-KH550 could be identified, the first stage from 200°C to 400°C was associated to the decomposition of the side groups of PAA-KH550 polymer. And the major weight loss in the second stage from 400°C to 650°C could be undoubtedly assigned to the decomposition of molecular chain of polymer. The final weight-loss ratio of PAA-KH550 polymer was about 95% in the end. Comparing the five traces, the weight

fraction of PAA-KH550 polymer on siloxane-GNPs and that of SiO₂ on SiO₂/GNPs hybrid material could be estimated by following equations [19]:

$$C\% = (1-X)*A\% + X*D\% \quad (1)$$

$$B\% = (1-Y)*C\% + Y*E\% \quad (2)$$

where A%, B%, C%, D%, and E% were the weight loss percentages at a certain temperature of f-GNPs, SiO₂/GNPs hybrid material, siloxane-GNPs, PAA-KH550, and SiO₂, respectively. X and Y were denoted as the weight fraction of polymeric species on siloxane-GNPs and content of SiO₂ on SiO₂/GNPs hybrid material, respectively.

According to our calculation, At 900°C, the residual weight fraction of polymer on siloxane-GNPs was about 94.2% and that of SiO₂ particles on hybrid materials was about 75.0%.

Scanning electron microscopy

Figure 5 presented the SEM micrographs of the morphology of various GNPs samples. f-GNPs in lateral

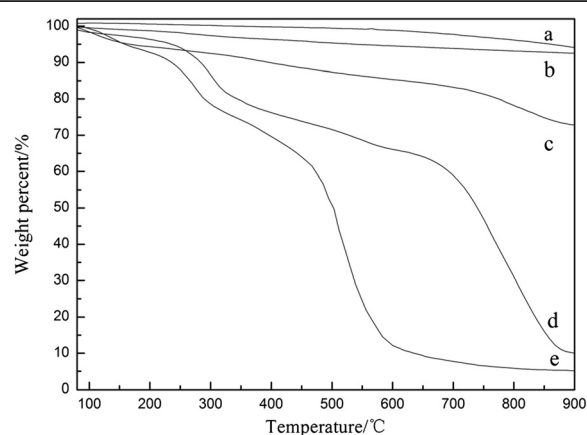


Figure 4 TGA curve spectrum diagram. (curve a) SiO₂, (curve b) f-GNPs, (curve c) SiO₂/GNPs hybrid material, (curve d) siloxane-GNPs, and (curve e) PAA-KH550.

Table 3 Intensity ratio of the D and G bands (I_D/I_G)

Samples	D area	G area	I_D/I_G
f-GNPs	257,462	316,479	0.814
SiO ₂ /GNPs	380,603	332,156	1.145

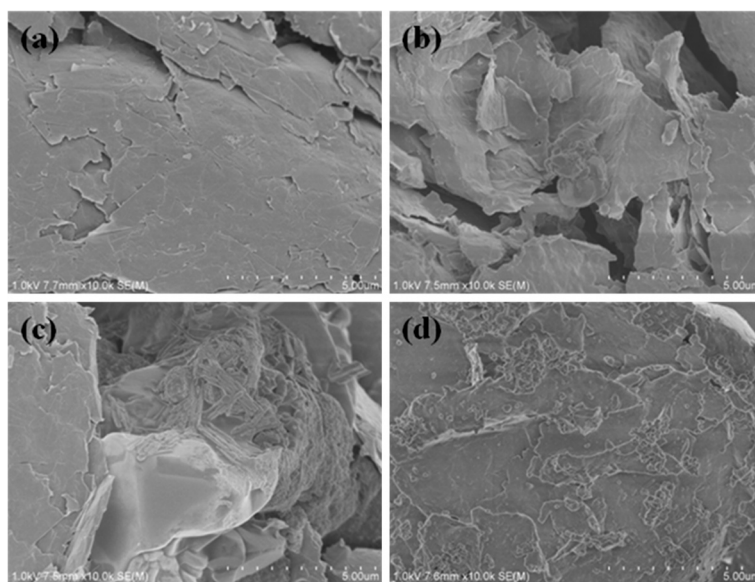


Figure 5 SEM images of (a) f-GNPs, (b) PAA-GNPs, (c) siloxane-GNPs and (d) SiO₂/GNPs.

dimension were shown in Figure 5a, which were crumpled due to the transformation from a planar sp^2 -hybridized to a distorted sp^3 -hybridized geometry during the oxidation process. As shown in Figure 5b, after reacted with PAA, the sheet of GNPs appeared thicker

in its thickness. Figure 5c showed micrographs of siloxane-GNPs. There appeared polymer on the surface of GNPs because of reacting with KH550. As showed in Figure 5d, SiO₂ particles were adsorbed on surface of f-GNPs nanosheets. From all the images and analysis

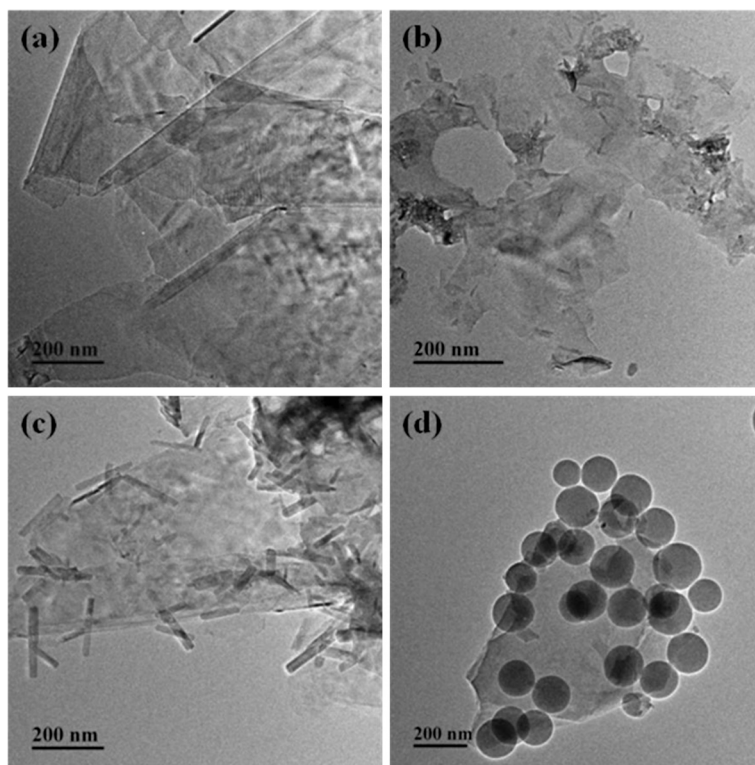


Figure 6 TEM images of (a) f-GNPs, (b) PAA-GNPs, (c) siloxane-GNPs, and (d) SiO₂/GNPs hybrid material.

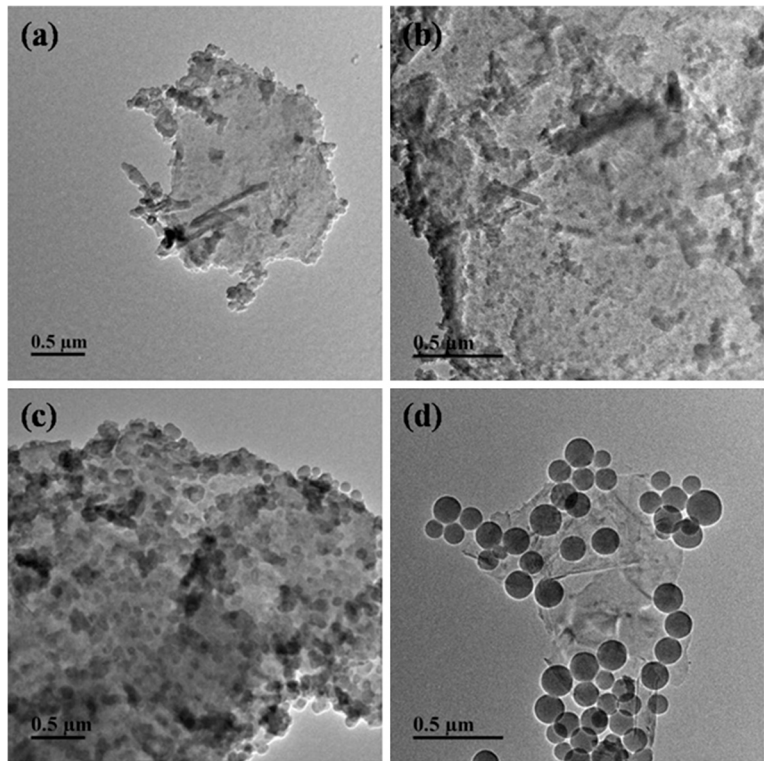


Figure 7 TEM images of the growing process of SiO₂/GNPs hybrid material with different times. (a) 2 h, (b) 4 h, (c) 6 h, and (d) 8 h.

above, it was reasonable to believe that SiO₂ particles have grown on the surface of GNPs successfully.

Transmission electron microscopy

The typical morphologies of all samples were observed with TEM. As shown in Figure 6a, the surface of f-GNPs was relatively smooth and clean. After being functionalized with PAA, the surface of GNPs became blurred as shown in Figure 6b. After reacted with KH550, the functionalized GNPs (Figure 6c) became thickened and there appeared tubes on the surface of GNPs. The typical morphologies of SiO₂/GNPs hybrid material were showed in Figure 6d. It was clear to discern that the SiO₂ particles were hanged on the surface of f-GNPs. And the diameter of SiO₂ varies from 100 to 200 nm. The TEM images were consistent with the result of the SEM, which confirmed that our route of preparing SiO₂/GNPs hybrid material was reasonable.

Figure 7 depicted the whole growth process of SiO₂ particles on the surface of graphene with the ammonia of 1.2 g and TEOS of 0.6 g. When the reaction time was 2 h (Figure 7a), we can see that graphene became thicker and there appeared polymeric substance on the surface of gra-phene. As the reaction time reached 4 h (Figure 7b), SiO₂ particles did not completely grow, but some little black points could be observed which were the miniatures of SiO₂ particles. With the time growing, it could be seen that the surface of graphene were covered with SiO₂

particles when the reaction time was 6 h (Figure 7c); SiO₂ particles became larger than that of Figure 7b, but had not completely grown to round shape. Figure 7d showed that after 8-h growing, SiO₂ particles had grown fully, and the average size of SiO₂ particles was 140 nm.

Analysis of orthogonal experiment

According to the matrix, nine experiments were carried out and the average size of SiO₂ particles was shown in Table 2. This table showed that the range of the size of SiO₂ particles varies from 50 to 280 nm; these data were taken as the original data and used in the range analysis. The mean values of Ij/kj, IIj/kj, and IIIj/kj for different

Table 4 Analysis of range of each other

Column no.	<i>j</i> = 1	2	3
Factors	TEOS	NH ₃ ·H ₂ O	Time
Ij	I1 = 310	I2 = 280	I3 = 380
IIj	II1 = 510	II2 = 520	II3 = 500
IIIj	III1 = 570	III2 = 590	III3 = 510
kj	k1 = 3	k2 = 3	k3 = 3
Ij/kj	103.3	93.3	126.7
IIj/kj	170	173.3	166.7
IIIj/kj	190	196.7	170
Range	86.7	103.4	43.3

factors at different levels in the range analysis were shown in Table 4. For each factor, a higher mean value indicates that the level has a larger effect on the size of SiO₂ particles. And the range value indicates the significance of the factor's effect, and a larger range means the factor has a bigger impact on the size of SiO₂ particles. Therefore, according to Table 4, compared with the range values of different factors, the factors' level of significance are as follows: ammonia (103.4) > TEOS (86.7) > reaction time (43.3). The range value of ammonia is the largest, which means that the quality of ammonia had the most important impact on the size of SiO₂ particles.

According to our analysis, the amount of ammonia affects the size of SiO₂ particles most. With the increasing of the amount of ammonia from 0.6 to 1.8 g, the size of SiO₂ particles increases continuously. The joining of ammonia can significantly contribute to the occurrence of hydrolysis and polycondensation reaction of TEOS. When adding NH₃·H₂O to the solution, the OH anion made the silicon atoms negatively charged. As a result, Si-O bond weakened and eventually cracked. The products of hydrolysis reaction such as Si-OH and Si-OR dehydration or dealcoholation in the next polycondensation processing form Si-O-Si chain. Si-O-Si chains cross-linked continuously with each other to fabricate SiO₂ particles finally. The hydrolysis rate will increase with the growing amount of ammonia, so the size of SiO₂ particles also becomes larger.

With the increasing of the amount of TEOS from 0.3 to 0.9 g, the size of SiO₂ particles also increases continuously. From the viewpoint of chemical equilibrium, the increasing of the content of TEOS contributes to the hydrolysis reaction to form SiO₂ particles. However, the influence of TEOS is not as significant as ammonia.

The reaction time also had impact on the results. The size of SiO₂ particles grew with the increasing of the reaction time from 4 to 8 h. With the time increasing, the cross-linking between Si-O-Si chains strengthened, and the size of SiO₂ particles became larger and larger.

According to the above analysis, the controllability of the particle sizes was realized and in a certain range, the quantity of ammonia, the quantity of TEOS and the reaction time all had positive effect on the growing of SiO₂ particles.

Conclusion

In this work, SiO₂/GNPs hybrid material had been successfully achieved by a facile and controllable method as designed. In this process, firstly, PAA was grafted to the surface of f-GNPs for providing reaction pots, and then KH550 reacted with abovementioned product PAA-GNPs to obtain siloxane-GNPs. Finally, the SiO₂/GNPs hybrid material is produced through introducing siloxane-GNPs into a solution of tetraethyl orthosilicate, ammonia, and ethanol for hours' reaction. The new characteristic band

from FTIR indicated that those chemical reactions had been occurred as designed, and the results from SEM and TEM indicated that SiO₂ nanoparticles were grown on the surface of f-GNPs successfully. Raman spectroscopy proved that after chemical drafting disordered, carbon atoms increased and carbon domains were destroyed. TGA traces suggested the residual weight fraction of polymer on siloxane-GNPs was about 94.2% and that of SiO₂ particles on hybrid materials was about 75.0% finally and the SiO₂/GNPs hybrid material we have prepared had stable thermal stability. Therefore, it was a feasible and reliable route to produce SiO₂/GNPs hybrid material. Through orthogonal experiments, we also got the result that the controllability of the particle sizes was realized and the amount of ammonia had the most important impact on the size of SiO₂ particles compared with quantity of TEOS and the reaction time. The next target of our study is to do research on the application of the hybrid material, to prepare epoxy resin composites with hybrid material, and study the influence of the SiO₂ particles' size to strengthen epoxy resin composites.

Abbreviations

APTES: 3-aminopropyltriethoxysilane; f-GNPs: functionalized graphene nanoplatelets; FTIR: Fourier transform infrared spectra; PAA: polyacrylic acid; SEM: scanning electron microscopy; SiO₂: silica nanoparticles; SiO₂/GNPs: SiO₂/graphene nanoplatelets; TEM: transmission electron microscopy; TGA: thermal gravimetric analysis.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

KY, KQ, HC, XL, and JS gave the guidance, JL did the experiments, analyzed the data, and gave the final approval of the version of the manuscript to be published. All authors read and approved the final manuscript.

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